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14. ABSTRACT Tailoring the chemical and physical properties of molecular materials by rational design to increase density, reduce toxicity, or to improve overall stability characteristics continues to be an important research endeavor. Achieving this by the structural modification of neutral organic compounds offers a limited scope of opportunities. Organic-like solid and liquid salts significantly enhance this flexibility for properties tailoring by pairing different classical heterocyclic cations with a plethora of different counteranions. Over the past 25 years, this is re-emphasized with salts based on neutral heterocyclic compounds. Rekindled interest in this approach appears to initiate with the unique properties exhibited by the hygroscopic binary 1-ethyl-3-methyl-1,3-imidazolium (EMIM) chloroaluminate salt <sup>1</sup> followed by a subsequent report of non-hygroscopic, air stable, binary EMIM salts containing other anions. <sup>2</sup> Later, triazolium cations are used to form salts with common anions. <sup>3</sup> We now report the synthesis and characterization of salts containing heterocyclic cations that are paired with two different three-dimensional polyhedral borane/carborane anions, [B <sub>12</sub> H <sub>12</sub> ] <sup>2-</sup> and [CB <sub>11</sub> H <sub>12</sub> ] <sup>-</sup> , as well as a new aqueous preparation method that does not require air-free techniques.					
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# Pairing Heterocyclic Cations with *c*loso-Icosahedral Borane and Carborane Anions. I. Benchtop Aqueous Synthesis of Binary Triazolium and Imidazolium Salts with Limited Water Solubility (Preprint)

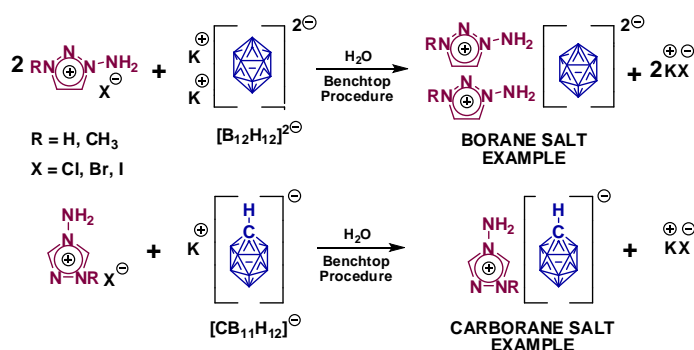
Scott A. Shackelford,<sup>\*</sup> John L. Belletire,<sup>†</sup> Jerry A. Boatz, Stefan Schneider, Amanda K. Wheaton,<sup>†</sup> Herman L. Ammon,<sup>‡</sup> and Steven H. Strauss<sup>§</sup>

*Air Force Research Laboratory, Propellants Branch (AFRL/RZSP), 10 East Saturn Blvd., Edwards AFB, CA 93524-7680, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, and Department of Chemistry, Colorado State University, Fort Collins, CO 80523*

scott.shackelford@edwards.af.mil

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## ABSTRACT



Ten new salts that pair triazolium and imidazolium cations with *c*loso-icosahedral anions [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> and [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> were synthesized in water solvent using an open-air, benchtop method. These unreported [Heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] and [Heterocyclium][CB<sub>11</sub>H<sub>12</sub>] salts extend reports of [Imidazolium][CB<sub>11</sub>H<sub>12</sub>] and [Pyridinium][CB<sub>11</sub>H<sub>12</sub>] salts that were synthesized in anhydrous organic solvents under an inert atmosphere with glovebox or Schlenk techniques. Spectroscopic data, melting points, and densities are reported for each salt. Single-crystal X-ray structures are provided for the five new [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> salts.

Tailoring the chemical and physical properties of molecular materials by rational design to increase density, reduce toxicity, or to improve overall stability characteristics continues to be an important research endeavor. Achieving this by the structural modification of neutral organic compounds offers a limited scope of opportunities. Organic-like solid and liquid salts significantly enhance this flexibility for properties tailoring by pairing different classical heterocyclic cations with a plethora of different counteranions. Over the past 25 years, this is re-emphasized with salts based on neutral heterocyclic compounds. Rekindled interest in this approach appears to initiate with the unique properties exhibited by the hygroscopic binary 1-ethyl-3-methyl-1,3-imidazolium (EMIM) chloroaluminate salt<sup>1</sup> followed by a subsequent report of non-hygroscopic, air stable, binary EMIM salts containing other anions.<sup>2</sup> Later, triazolium cations are used to form salts with common anions.<sup>3</sup>

We now report the synthesis and characterization of salts containing heterocyclic cations that are paired with two different three-dimensional polyhedral borane/carborane anions,  $[B_{12}H_{12}]^{2-}$  and  $[CB_{11}H_{12}]^{-}$ , as well as a new aqueous preparation method that does not require air-free techniques. These unique salts are comprised of aromatic planar  $\pi$ -delocalized cations and aromatic polyhedral  $\sigma$ -delocalized anions. Triazolium and imidazolium cations paired with the *closo*-icosahedral, weakly nucleophilic  $[B_{12}H_{12}]^{2-}$  di-anion represent the first reported examples of these borane salts **1-5**.

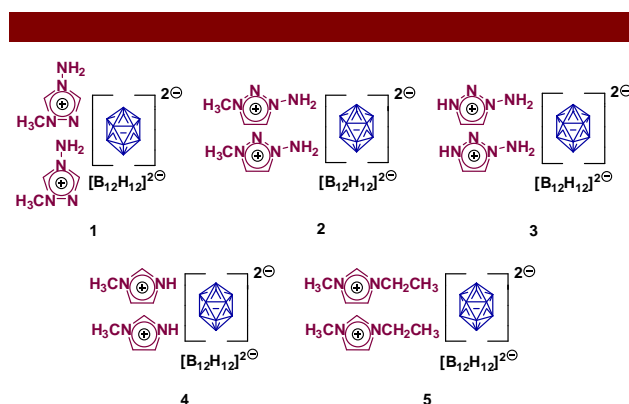
The  $[B_{12}H_{12}]^{2-}$  di-anion, first synthesized in 1960 as the triethylammonium salt,<sup>4</sup> is known to form salts of low toxicity and high thermal stability<sup>5</sup> and is purported to be the most stable covalently bonded chemical entity in all of chemistry.<sup>6a</sup> It is a “super-aromatic” polyhedral-shaped “counterpart of the planar benzene molecule with 26 delocalized valence electrons in its  $\sigma$ -bonded framework”<sup>6</sup> and possesses an overall negative two charge. This unique  $[B_{12}H_{12}]^{2-}$  dianion is paired with either two planar aromatic triazolium or two imidazolium cations, which each possess six delocalized valence electrons in its  $\pi$ -bonded cyclic structure and an overall negative one charge. These new  $[\text{Heterocyclium}]_2[B_{12}H_{12}]$  salts **1-5** previously have not been reported. The icosahedral monoanion, *closo*- $[CB_{11}H_{12}]^{-}$ , first reported in 1967,<sup>7</sup> also forms thermally stable salts. Analogous  $[\text{Triazolium}][CB_{11}H_{12}]$  **6-9** and one new  $[\text{Imidazolium}][CB_{11}H_{12}]$  **10** salts also are described which extend properties characterization beyond several  $[\text{Imidazolium}][CB_{11}H_{12}]$ <sup>8</sup> and one  $[\text{Pyridinium}][CB_{11}H_{12}]$ <sup>9</sup> salts that previously were reported.

The former  $[\text{Imidazolium}][CB_{11}H_{12}]$  salts were prepared by stirring the  $Cs^+$  or  $Ag^+$  salt of  $[CB_{11}H_{12}]^{-}$  with the appropriate imidazolium halide in an *anhydrous organic solvent, or mixture of solvents, inside an inert-atmosphere glovebox* for 10 h. The solid phase  $CsCl$  or  $AgCl$  byproduct was separated from the supernatant by filtration through Celite. Removal of solvent afforded white crystals.<sup>8</sup> The  $[N\text{-Pentylpyridinium}][CB_{11}H_{12}]$  salt

was prepared similarly over 20 h using *Schlenk air-free techniques* and column chromatography purification.<sup>9</sup>

In contrast, this first paper describes heterocyclium borane/carborane salts that are relatively water insoluble at rt where a high water solubility of the potassium halide byproduct is advantageous. Our aqueous-based metatheses require reaction times of only several minutes and are conducted in a benchtop fumehood with standard glassware open reaction vessels and deionized (DI) water solvent. With the relatively low water solubilities exhibited by the heterocyclium salts of  $[B_{12}H_{12}]^{2-}$  **1-5** and  $[CB_{11}H_{12}]^{-}$  **6-11**, anhydrous solvents can be avoided and air-stable products obtained. Because all the heterocyclium halides used in this work, as well as the  $K_2[B_{12}H_{12}]$  and  $K[CB_{11}H_{12}]$  reactant salts,<sup>10</sup> are water soluble, reactions are rapid. The two reagents are mixed in stoichiometric amounts, and precipitation or slow recrystallization yields the desired salt product **1-11**<sup>11</sup> which are readily separated from the potassium halide-containing aqueous supernatant by filtration and washing with cold DI water. Crude product yields are in the 71% to 96% range. Recrystallization from hot DI water, in some cases containing a small proportion of methanol, removes any small amounts of potassium and halide ions to give overall yields ranging from 44% to 84%. A trace of the residual potassium cation should not afford the catalysis problems sometimes caused by trace silver cations following a silver salt metathesis.

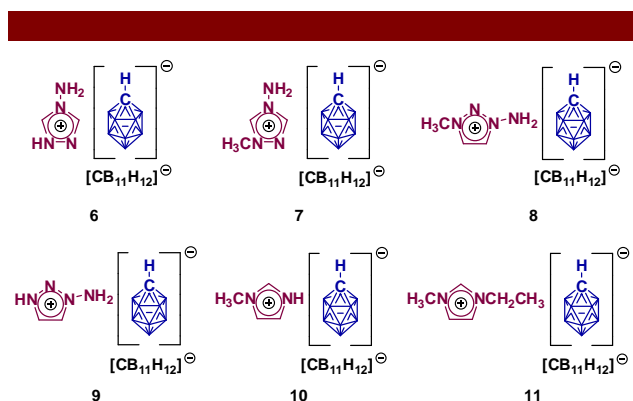
Figure 1 displays the five heterocyclinium borane salts synthesized by our benchtop, open-air, aqueous procedure. The synthesis and spectroscopic data for  $[4\text{-Amino-1-methyl-1,2,4-triazolium}]_2[B_{12}H_{12}]$  **1** are typical.<sup>12</sup> More detailed syntheses for **1** and for the four other  $[B_{12}H_{12}]^{2-}$  salts, 1-amino-3-methyl-1,2,3-triazolium borane **2**, 1-amino-3-H-1,2,3-triazolium borane **3**, 1-methylimidazolium borane **4**, and 1-ethyl-3-methylimidazolium borane **5**, appear in the supporting information (SI).



**Figure 1.**  $[\text{Heterocyclium}]_2[B_{12}H_{12}]$  Borane Salts Prepared.

Figure 2 shows the six new  $[\text{Heterocyclium}][CB_{11}H_{12}]$  salts synthesized, 4-amino-1-H-1,2,4-triazolium carborane **6**, 4-amino-1-methyl-1,2,4-triazolium carborane **7**, 1-

amino-3-methyl-1,2,3-triazolium carborane **8**, 1-amino-3-H-1,2,3-triazolium carborane **9**, 1-methylimidazolium carborane **10**, and 1-ethyl-3-methylimidazolium carborane **11**. The synthesis of [1-Amino-3-H-1,2,3-triazolium][CB<sub>11</sub>H<sub>12</sub>]<sup>−</sup> **9** is typical.<sup>13</sup> More detailed [Heterocyclium][CB<sub>11</sub>H<sub>12</sub>]<sup>−</sup> salt syntheses for salts **6-11** appear in the SI.



**Figure 2.** [Heterocyclium][CB<sub>11</sub>H<sub>12</sub>]<sup>−</sup> Carborane Salts Prepared.

Initial syntheses were conducted on a small 150-200 mg scale based on K<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>]<sup>2−</sup> and K[CB<sub>11</sub>H<sub>12</sub>]<sup>−</sup>. Once optimum conditions were determined for each salt, the metathesis reactions were conducted on a 1-4 g scale. The [B<sub>12</sub>H<sub>12</sub>]<sup>2−</sup> salt of **3** was directly scaled from 2 g to 5.5 g for K<sub>2</sub>[B<sub>11</sub>H<sub>12</sub>]<sup>−</sup> with a comparable yield and final purity.

The density, melting point, and reaction yields for salts **1** to **11** are listed in Tables 1-3. Experimental densities are obtained by pycnometry at rt and are compared to a newly-developed predictive density additivity code<sup>14</sup> that initially was updated for heterocyclium *closo*-icosahedral borane and carborane salts. This updated code predicts an average 2.0% variance from the 11 pycnometry-based density values. Density differences range from 4.2% with salt **6** to 0% with salts **7** and **9**. Pycnometry densities for salts **2** and **3** do not contain occluded solvent molecules which are present in the single crystal X-ray analyses.<sup>15</sup>

An X-ray crystal packing structure of [4-Amino-1-methyl-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>]<sup>2−</sup> **1** appears in Figure 3. Single crystal X-ray data for [Heterocyclium][B<sub>12</sub>H<sub>12</sub>]<sup>2−</sup> salts **1-5** are found in the SI.<sup>15</sup> Melting points are obtained in open capillary tubes and are uncorrected. Both the crude and overall product yield are given for each salt in Tables 1-3. This overall yield is determined by multiplying the crude yield percent with the percentage of salt product recovered after recrystallization.

The previously reported [1-Ethyl-3-methylimidazolium][CB<sub>11</sub>H<sub>12</sub>]<sup>−</sup> salt **11** was synthesized by a silver salt-based metathesis procedure.<sup>8</sup> The earlier measured X-ray single crystal density of 1.07 g/cc compares well with our pycnometry density of 1.03 g/cc, taken at rt, and the predicted density<sup>14</sup> of 1.05 g/cc (Table 3). Our visually-determined melting point (1 °C/min) is 175-176 °C compared to the reported DSC-based melting

point of 122 °C.<sup>8</sup> Apparently, an endothermic DSC peak at 122 °C was taken to be a melting point.<sup>16</sup> Our yields of 94% (crude), 74% (recrystallized), and 70% (overall) compare favorably with the 90% yield previously reported for salt **11**.<sup>8</sup>

**Table 1.** 4-Amino-1,2,4-Triazolium Borane & Carborane Salts.

[H <sub>2</sub> N-N <sup>+</sup> (CH <sub>3</sub> )-N <sub>3</sub> ] <sup>+</sup> n	[B <sub>12</sub> H <sub>12</sub> ] <sup>2−</sup> n = 2	[CB <sub>11</sub> H <sub>12</sub> ] <sup>−</sup> n = 1	Melting Point (°C) Density (g/cc)	Yields (%)
			pycnometry / X-ray (predicted)	Direct Ppt. (Overall)
1: X = CH <sub>3</sub>	Borane	—	181-182 1.22 / 1.24 (1.20)	91.0 (79.7)
6: X = H	—	Carborane	260-262 1.19 / --- (1.14)	71.0 (43.5)
7: X = CH <sub>3</sub>	—	Carborane	161-162 1.12 / --- (1.12)	92.0 (65.5)

**Table 2.** 1-Amino-1,2,3-Triazolium Borane & Carborane Salts.

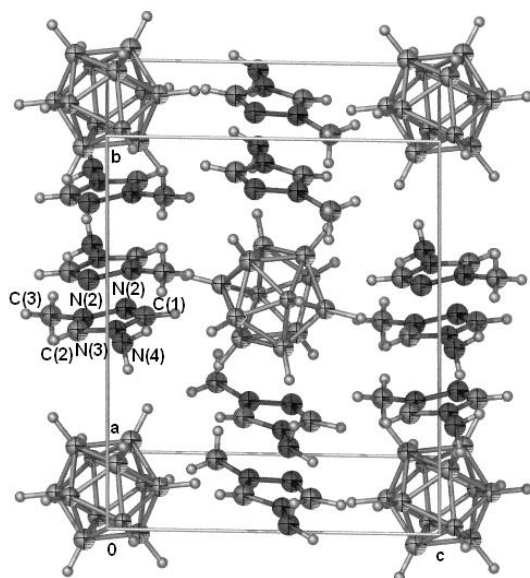
[H <sub>2</sub> N-N <sup>+</sup> (CH <sub>3</sub> )-N <sub>3</sub> ] <sup>+</sup> n	[B <sub>12</sub> H <sub>12</sub> ] <sup>2−</sup> n = 2	[CB <sub>11</sub> H <sub>12</sub> ] <sup>−</sup> n = 1	Melting Point (°C) Density (g/cc)	Yields (%)
			pycnometry / X-ray (predicted)	Direct Ppt. (Overall)
2: X = CH <sub>3</sub>	Borane	—	199-218 <sup>a</sup> 1.19 / 1.13 <sup>(15)</sup> (1.18)	78.2 (66.7)
3: X = H	Borane	—	148-152 <sup>a</sup> 1.26 / 1.27 <sup>(15)</sup> (1.27)	76.4 (61.1)
8: X = CH <sub>3</sub>	—	Carborane	259-262 1.10 / --- (1.14)	95.8 (76.5)
9: X = H	—	Carborane	182-183 <sup>a</sup> 1.16 / --- (1.16)	70.8 (54.9)

a. Melts with gas evolution.

The [4-Amino-1H-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>]<sup>2−</sup> salt, analogous to [CB<sub>11</sub>H<sub>12</sub>]<sup>−</sup> salt **6**, is absent from Table 1. Unique challenges surfaced in its synthesis. Treating it like water soluble binary triazolium and tetrazolium borane/carborane salts encountered in this research effort was the answer. These will be reported in a future publication as well as an option for pairing equimolar amounts of two dissimilar heterocyclic cations with the [B<sub>12</sub>H<sub>12</sub>]<sup>2−</sup> di-anion to give mixed heterocyclium borane salts. Initial results have given three such mixed cation borane salts: e.g. [4-Amino-1-methyl-1,2,4-triazolium][1-Ethyl-3-methylimidazolium][B<sub>12</sub>H<sub>12</sub>]<sup>2−</sup> using the heterocyclic cations seen in salts **1** and **11**.

**Table 3.** Imidazolium Borane & Carborane Salts.

$\left[ \text{XN}^{\oplus}\text{NY} \right]^n$	$\left[ \text{B}_{12}\text{H}_{12} \right]^{2\ominus}$ n = 2	$\left[ \text{CB}_{11}\text{H}_{11} \right]^{\ominus}$ n = 1	Melting Point (°C) Density (g/cc) pychnometry / X-ray (predicted)	Yields (%) Direct Ppt. (Overall)
4: X = CH <sub>3</sub> Y = H	Borane	—	260-262 <sup>a</sup> 1.08 / 1.11 (1.12)	82.3 (60.0)
5: X = CH <sub>3</sub> Y = CH <sub>2</sub> CH <sub>3</sub>	Borane	—	290-292 <sup>a</sup> 1.06 / 1.10 (1.08)	81.6 (74.2)
10: X = CH <sub>3</sub> Y = H	—	Carborane	368-369 <sup>a</sup> 1.11 / --- (1.07)	93.2 (83.5)
11: X = CH <sub>3</sub> Y = CH <sub>2</sub> CH <sub>3</sub>	—	Carborane	175-176 <sup>a, (16)</sup> 1.03 / --- (1.05)	93.6 (69.5)

**Figure 3.** Crystal Packing of Salt 1 Viewed Along the Crystallographic *a*-Axis.

**Acknowledgment.** Thank you to AFRL/RZS, Edwards AFB, CA, for welcome administrative, financial, and technical support.

**Supporting Information Available:** Experimental procedures, <sup>1</sup>H/<sup>13</sup>C NMR and FTIR spectroscopy data, detailed melting point notes for salts 1-11, single crystal X-ray for salts 1-5 in .cif-format, and HRMS for salts 6-11. This material is available free of charge via the Internet at <http://pubs.acs.org>.

† ERC, Inc. contractor at AFRL/RZSP, Edwards AFB.

‡ University of Maryland, College Park, MD.

§ Colorado State University, Ft. Collins, CO.

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(10) The K<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> and K[HCB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> reactants were purchased: Katchem Ltd., E. Krasnohorská 6, 110 00 Prague 1, Czech Republic and were used as received.

(11) Depending upon the salt product solubility, some heterocyclinium salts immediately precipitate; in other cases, the desired heterocyclinium salt crystallizes overnight at +3.5 °C.

(12) [4-Amino-1-methyl-1,2,4-triazolium][*closo*-B<sub>12</sub>H<sub>12</sub>], **1**: Solid [4-Amino-1-methyl-1,2,4-triazolium] iodide (4.52 g; 20.00 mmol; CH<sub>3</sub>I methylated plus recrystallization from methanol) and commercial K<sub>2</sub>[*closo*-B<sub>12</sub>H<sub>12</sub>] (2.20 g; 10.00 mmol) were placed into a 50 mL beaker. To this was added 18.0 mL DI water. The contents were stirred and heated at gentle reflux for 4 min. The resulting clear tan solution was cooled overnight in a refrigerator and off-white crystals deposited. Filtration and rinsing the filter-cake with 2 x 1.0 mL portions of pre-chilled DI water followed. The crystals were dried under high vacuum to give anhydrous spectroscopically pure salt product by <sup>1</sup>H NMR (3.096 g; 91.05%). Recrystallization of a portion (1.04 g) was conducted in 40.0 mL boiling DI water containing 5 mL anhydrous methanol. Most of the methanol boiled off. The resulting clear solution was cooled overnight in a refrigerator (3.5 °C) to give nicely formed crystals. Filtration, washing the crystals with 0.5 mL of pre-chilled DI water, and drying at 65 °C under high vacuum (50 mTorr) in a Chem-Dry™ apparatus over 72 h gave 0.91 g white solid; (recrystallized portion = 87.6% recovery); overall purified yield = 79.7%: <sup>1</sup>H NMR 400 MHz, std. DMSO-d<sub>6</sub> (2.51): δ 10.04 (s, 2H), 9.15 (s, 2H), 6.92 (s, 4H), 4.04 (s, 6H), 1.70-0.10 (complex m, 12H); <sup>13</sup>C NMR (100 MHz, std. DMSO-d<sub>6</sub> (39.51): δ 145.05, 142.92, 38.97; FTIR (HATR) 3350, 3309, 3252, 3220, 3134, 3093, 2978, 2472, 2447, 1585, 1479, 1462, 1442, 1254, 1201, 1164, 1123, 1062, 988, 882, 850, 792, 711, 657, 621, 600, 568 cm<sup>-1</sup>; X-ray in Fig. 3 and supplemental information.

(13) [1-Amino-3-H-1,2,3-triazolium][*closo*-HCB<sub>11</sub>H<sub>11</sub>], **9**: Solid [1-Amino-3-H-1,2,3-triazolium] chloride (2.41g; 20.00 mmol and commercial K[*closo*-HCB<sub>11</sub>H<sub>11</sub>]] (3.64 g; 20.01 mmol) are placed into a 50 mL Pyrex beaker. Addition of 10.0 mL DI water was followed by heating to gentle reflux and then pouring the nearly clear solution into a fresh 50 mL Pyrex beaker leaving behind a small amount of a water insoluble impurity in the K[*closo*-HCB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> reactant. The reaction mixture was cooled overnight in the refrigerator (3.5 °C) to effect crystallization. Filtration, rinsing the filter-cake with 2.0 mL of pre-chilled DI water, and pumping at high vacuum (60 mTorr) gave a 4.59 g of solid with some entrained water. Two recrystallizations from 7.0 mL refluxing DI water gave 2.51 g of pure salt; overall purified yield (two recrystallizations) = 54.9%: <sup>1</sup>H NMR 400 MHz, std. DMSO-d<sub>6</sub> (2.50): δ 8.71 (brs, 3H), 7.96 (d, J = 1.1 Hz, 1H), 7.74 (d, J = 1.1 Hz, 1H), 2.39 (brs, 1H), 2.25-0.75 (complex m, 11H); <sup>13</sup>C NMR (100 MHz, std. DMSO-d<sub>6</sub> (39.51): δ 132.09, 124.28, 50.79; FTIR (HATR) 3714, 3694, 3653, 3636, 3346, 3264, 3154, 3134, 2521, 1659, 1605, 1540, 1462, 1442, 1299, 1168, 1111, 1078, 1017, 956, 890, 788, 711, 694, 657, 625, 600, 564, 543 cm<sup>-1</sup>; HRMS calcd for [M - 3H]<sup>+</sup> m/z = 225.2315, found 225.2325; calcd for [HCB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> m/z = 143.2035, found 143.2045.

(14) Ammon, H. L. *Propellants, Explos., Pyrotech.* **2008**, *33*, 92.

(15) Preparing acceptable single crystals for X-ray analysis results in two occluded CH<sub>3</sub>CN molecules for salt **2** and two occluded H<sub>2</sub>O molecules for salt **3**. Both salts become amorphous powders when the solvent molecules are removed for pycnometry density analyses.

(16) Our DSC analyses of salt **11** (1 °C/min) show a small endotherm at 125 °C, which we attribute to a solid phase transition, and a larger endotherm at 175-176 °C. This latter temperature matches the visually-determined melting point where a white solid changes to a colorless liquid. Visually-determined solid softening occurs from 106-132 °C.



# Pairing Heterocyclic Cations with *closo*-Icosahedral Borane and Carborane Anions. I. Benchtop Aqueous Synthesis of Binary Triazolium and Imidazolium Salts with Limited Water Solubility

Scott A. Shackelford,\* John L. Belletire,<sup>†</sup> Jerry A. Boatz, Stefan Schneider, Amanda K. Wheaton,<sup>†</sup> Herman L. Ammon,<sup>‡</sup> and Steven H. Strauss<sup>§</sup>

*Air Force Research Laboratory, Propellants Branch (AFRL/RZSP), 10 East Saturn Blvd., Edwards AFB, CA 93524-7680, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, and Department of Chemistry, Colorado State University, Fort Collins, CO 80523*

*scott.shackelford@edwards.af.mil*

## SUPPLEMENTAL INFORMATION

### References

<sup>†</sup> ERC, Inc. contractor at AFRL/RZSP, Edwards AFB, CA (USA).

<sup>‡</sup> Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.

<sup>§</sup> Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

(1) – (16) appear in the main paper.

(17) See under **X-ray Analyses** section below.

(18) Kaplan, G.; Drake, G.; Tollison, K.; Hall, L.; Hawkins, T. *J. Heterocyclic Chem.* **2005**, 42, 19.

## Experimental

All neutral heterocycles, that were converted to either a hydrochloride or methyl iodide reactant salt for the metathesis reactions outlined, were purchased commercially with one exception. The 1-amino-1,2,3-triazole compound, synthesized as described in reference 16, was converted without further purification. The 1-ethyl-3-methylimidazolium bromide was purchased commercially. Deionized (DI) water was obtained from an in-house Millipore MILL-Q Reagent Grade Water System at an 18 megaohm cm purity level. All organic solvents were commercially purchased, were either Reagent Grade or HPLC purity, and were used as received.

With regard to salt product purity, the only major impurity would be the potassium halide co-product. All salts are spectroscopically pure by NMR. While we have an in-house elemental analysis capability, we found it difficult to achieve complete combustion with these salts and obtained inconclusive results. High Resolution MS was used in-lieu of elemental analyses for the heterocyclium carborane salts, but was not conclusive for the analogous boranes. Instead, single crystal X-ray analyses were accomplished on the heterocyclium boranes. After one water recrystallization, we estimate a 99% purity for all salts. Salt **3** serves as an example. Because borane salt **3** is the most water soluble in this series, to minimize product losses, its first recrystallization was from a methanol/ethyl acetate co-solvent and gave a 94<sup>+</sup>% purity (KCl impurity) by ICP analysis. Following a subsequent water recrystallization, this purity improved to 99.9% by ICP analysis, but with a significant reduction in recrystallized borane salt **3**.

**NMR Data.** A Bruker Avance 400 Digital NMR instrument was used to obtain both proton (<sup>1</sup>H) and <sup>13</sup>C spectra.

**FTIR Data.** Fourier transform infra red spectra (FTIR) were taken as powder samples using a Nicolet 6700 Spectrometer in air using with an HATR optical system.

**High Resolution Mass Spectrometry Analyses.** High resolution mass spectra (HRMS) analyses were conducted at UCR Mass Spectrometry Facility, Department of Chemistry, University of California, 501 Big Springs Road (CS1), Riverside, CA 92521, Dr. Richard W. Kondrat, Academic Coordinator, and Mr. Ronald B. New, Staff Research Associate. Negative mode HRMS values for the [cation/anion – 3H] carborane clusters and for the [CB<sub>11</sub>H<sub>12</sub>]<sup>–</sup> anion in each carborane salt **6-11** gave acceptable exact masses. Borane salt **5** gave an acceptable exact mass variance (0 ppm) in the HRMS negative mode for a [cation/anion – 2H] cluster, but not for any [cation<sub>2</sub>/anion] borane cluster, nor for its [B<sub>12</sub>H<sub>12</sub>]<sup>2–</sup> di-anion. Borane salts **1-4** displayed no exact mass values within an acceptable variance, and therefore, are verified by single crystal X-ray analysis along with borane salt **5**.

**X-ray Analyses.** The single-crystal X-ray diffraction data were collected on a Bruker 3-circle-platform diffractometer equipped with a SMART APEX 2 detector with the  $\chi$ -axis fixed at 54.74° and using MoK $\alpha$  or CuK $\alpha$  radiation from a fine-focus tube. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. The data collection as well as structure solution and refinement were carried out using standard procedures with the APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, and SHELXTL software packages and programs<sup>17</sup>. Crystal data

and refinement details of crystals of **1-5** are given in Table 1-5. Crystallographic data are also available in CIF-format.

(17) APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, SHELXTL ed.; Bruker-AXS, INC.: Madison, WI USA, 2007.

**DSC Analyses.** Differential scanning calorimetry (DSC) thermograms for product salt **11** were taken on a Universal V4.1D TA instrument using hermetically sealed Al pans (pan #900793.90; lid #900794.901) and a 1 °C per minute temperature ramp. A detailed description of all reaction procedures and purification methods follow.

**Melting Point Data.** Visually-determined melting point values come from a Stanford Research Systems OptiMelt MPA100-Automated Melting Point Apparatus equipped with digital image video playback software. Observed melting point behavior tends to differ somewhat from what is seen with neutral covalent organic compounds; so, more detail is provided in **Table 6** at the end of this section.

### Synthesis Procedures.

**[4-Amino-1-methyl-1,2,4-triazolium]<sub>2</sub> [closo-B<sub>12</sub>H<sub>12</sub>] (1):** Solid [4-Amino-1-methyl-1,2,4-triazolium] iodide (4.52 g; 20.00 mmol; limiting reagent; prepared from commercial (Aldrich) 4-amino-1,2,4- triazole as a tan solid after prolonged treatment at rt with excess. iodomethane in methanol (protected from direct light), removal of volatiles, plus recrystallization from methanol) and commercial K<sub>2</sub>[closo-B<sub>12</sub>H<sub>12</sub>] (2.20 g; 10.00 mmol) were placed into a 50 mL beaker. To this was added 18.0 mL DI water. The contents were stirred (glass stirring rod) and heated at gentle reflux for 4 min on a hot plate. The resulting clear tan solution was cooled overnight in a refrigerator (3.5 °C) and a mass of off-white crystals deposited. The crystals were stirred several times after crystallization began. Filtration was followed by rinsing the filter-cake with 2 x 1.0 mL portions of pre-chilled DI water. The crystals were dried overnight to an off-white powder in a tarred flask under high vacuum (50 mTorr) with occasional application of a heat gun to afford anhyd material that was spectroscopically pure by <sup>1</sup>H NMR (3.10 g; 91.0%). Recrystallization of a portion (1.04 g) of the salt was conducted in boiling DI water (40.0 mL) containing anhydrous methanol (5.0 mL). Most of the methanol was then boiled off. The resulting clear solution was cooled overnight in a refrigerator (3.5 °C) to provide nicely formed crystals. Filtration, washing the crystals with 0.5 mL of pre-chilled DI water, and drying under high vacuum (50 mTorr) in a Chem-Dry™ apparatus (held at 65 °C) over 72 h gave a white solid; 0.910 g; recovery from the DI water recrystallized sub-portion = 87.6%; overall yield from initial limiting reagent to purified compound = 79.7% (mp = 181-182 °C): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.51) δ 10.04 (s, 2H), 9.15 (s, 2H), 6.92 (s, 4H), 4.04 (s, 6H), 1.70-0.10 (complex unresolved m, 12H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51) δ 145.05, 142.92, 38.97; FTIR (HATR method; significant peaks) 3350, 3309, 3252, 3220, 3134, 3093, 2978, 2472, 2447, 1585, 1479, 1462, 1442, 1254, 1201, 1164, 1123, 1062, 988, 882, 850, 792, 711, 657, 621, 600, 568 cm<sup>-1</sup>.

**Table 1.** Crystal and structure refinement data for **1**.

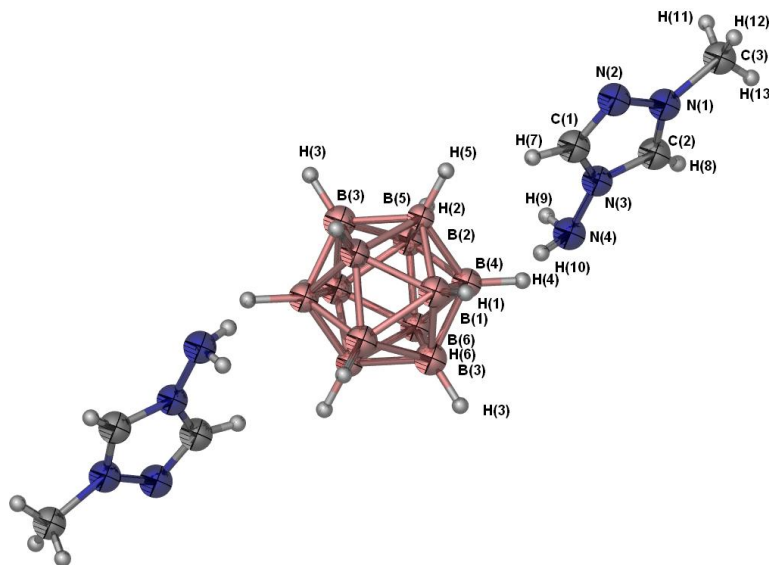
(1) (M4AT) <sub>2</sub> B <sub>12</sub> H <sub>12</sub>
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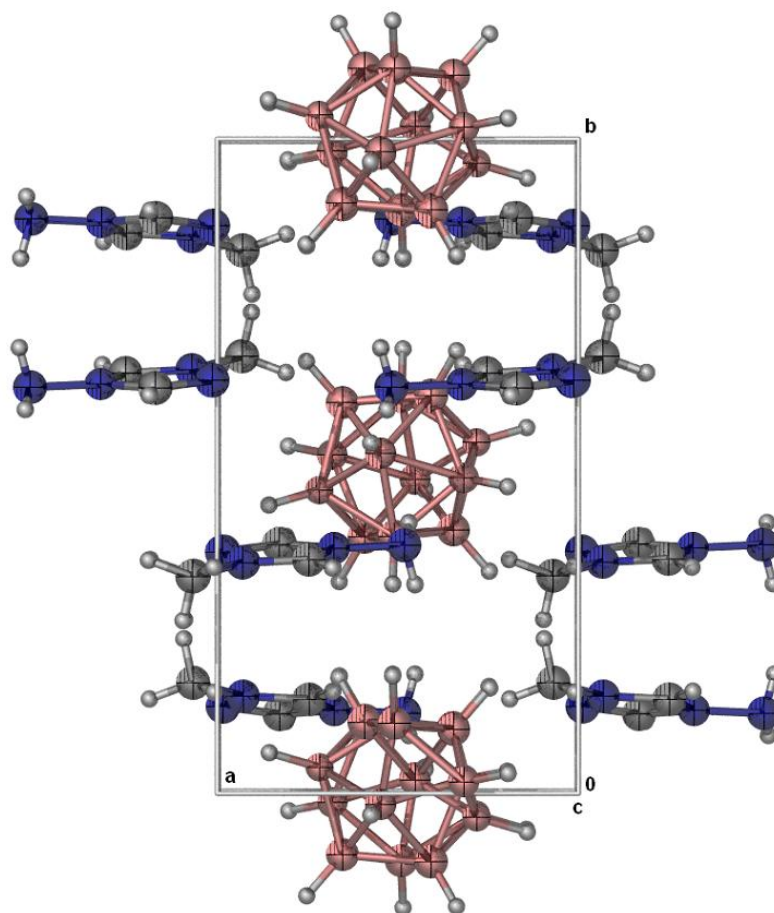
Formula	B <sub>12</sub> H <sub>12</sub> , 2(C <sub>3</sub> H <sub>7</sub> N <sub>4</sub> )
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> monoclinic
<i>a</i> (Å)	7.036(6)
<i>b</i> (Å)	12.707(10)
<i>c</i> (Å)	10.176(8)
β (°)	93.001(10)
<i>V</i> /Å <sup>3</sup>	908.6(13)
ρ <sub>calc.</sub> /g cm <sup>-3</sup>	1.243
<i>Z</i>	2
Formula weight	340.07
μ/mm <sup>-1</sup>	0.071
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.27x0.26x0.19
Theta range θ/°	2.57 to 25.46
Index range	-8≤ <i>h</i> ≤8, -15≤ <i>k</i> ≤15, -11≤ <i>l</i> ≤12
Reflection collected	6528
Independent [R(int)]/	1697 [0.0746]
Obs. refl. ([I > 2.0 σ(I)])	1277
F(000)	356
GooF	1.030
R <sub>1</sub> , wR [I > 2σ(I)]	0.0657, 0.1723
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.0831, 0.1921
L.diff. peak/hole eÅ <sup>-3</sup>	0.38 and -0.25
Absorption correct.	multiscan SADABS
T <sub>min</sub> , T <sub>max</sub>	0.981, 0.987
Data/restraints/param.	1697/0/170
Refinement method	Full-matrix least squares on F <sup>2</sup>

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; R_2 = \{ \sum [w(|F_o|^2 - |F_c|^2)^2] / \sum (w|F_o|^2)^2 \}^{1/2}$$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure 1.** Molecular drawing of **1**. Thermal ellipsoids are shown at 50% probability level.



**Figure 2.** Crystal packing of **1** viewed along the *c*-axis.

**[1-Amino-3-methyl-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] (2):** Solid [1-Amino-3-methyl-1,2,3-triazolium] iodide (5.70 g;  $\leq 25.20$  mmol; made as described above from known<sup>18</sup> 1-amino-1,2,3-triazole free base) was weighed into a 50 mL Pyrex beaker. Commercial K<sub>2</sub>[*closo*-B<sub>12</sub>H<sub>12</sub>] (2.77g; 12.60 mmol; limiting reagent) was then placed in the same beaker. To this was added 8.0 mL of DI water. While stirring with a glass stirring rod, the reaction mixture was brought to a gentle reflux for 4 min on a hot plate to afford a clear brownish-yellow solution. The contents of the beaker were allowed to cool for several days in the refrigerator (3.5 °C). The mass of crystals was filtered, rinsed with 1.5 mL of pre-chilled DI water, and dried at high vacuum (50 mTorr) in a tared flask to afford beige crystals. The crude solid (3.35 g; 78.2%) was spectroscopically pure by <sup>1</sup>H NMR. Purified material was obtained by a recrystallization of a portion (3.30 g) of the isolated solid from 9.0 mL of DI water at reflux followed by slowly cooling overnight in the refrigerator (3.5 °C). The filtered crystals were rinsed with 1.0 mL of pre-chilled DI water and pumped at high vacuum (50 mTorr) in a tared flask to provide a beige solid; 2.82 g; recovery from the DI water recrystallized sub-portion = 85.3%; overall yield from limiting reagent starting material to purified product =

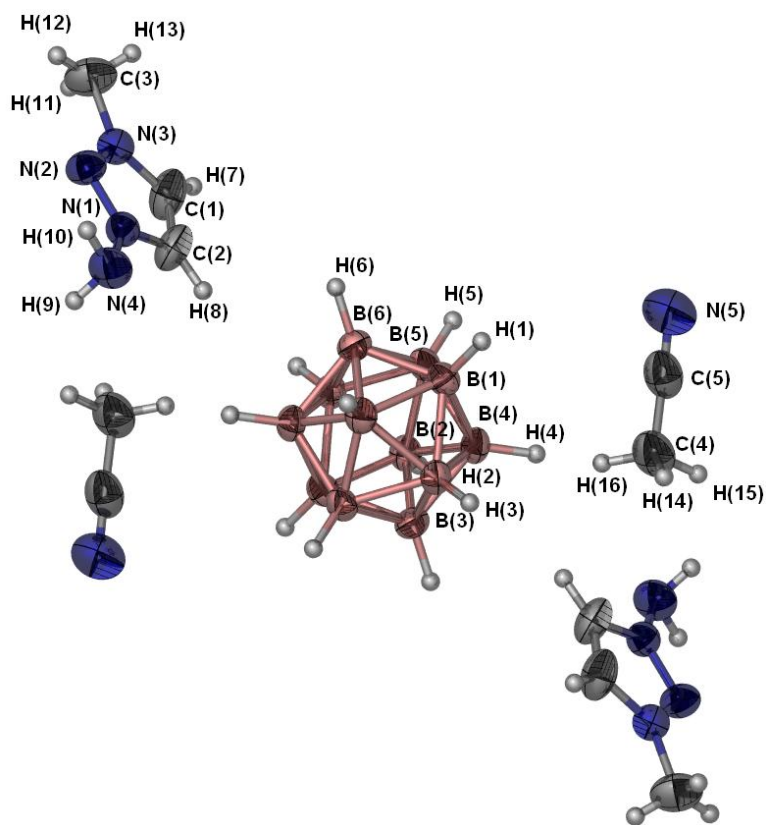
66.7% (mp = 199-218 °C with slow gas evolution): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.51) δ 8.73 (d, J = 1.2 Hz, 2H), 8.60 (d, J = 1.2 Hz, 2H), 8.25 (brs, 4H), 4.23 (s, 6H), 1.70-0.10 (complex m 12H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51) δ 131.54, 126.89, 39.75; FTIR (HATR method; significant peaks) 3632, 3596, 3575, 3465, 3342, 3322, 3264, 3240, 3203, 3126, 3109, 3036, 2537, 2468, 2263, 2124, 2096, 2022, 1965 1622, 1601, 1585, 1569, 1528, 1446, 1377, 1213, 1095, 1062, 1025, 911, 801, 715, 662, 600, 572 cm<sup>-1</sup>.

**Table 2.** Crystal and structure refinement data for **2·2CH<sub>3</sub>CN**.

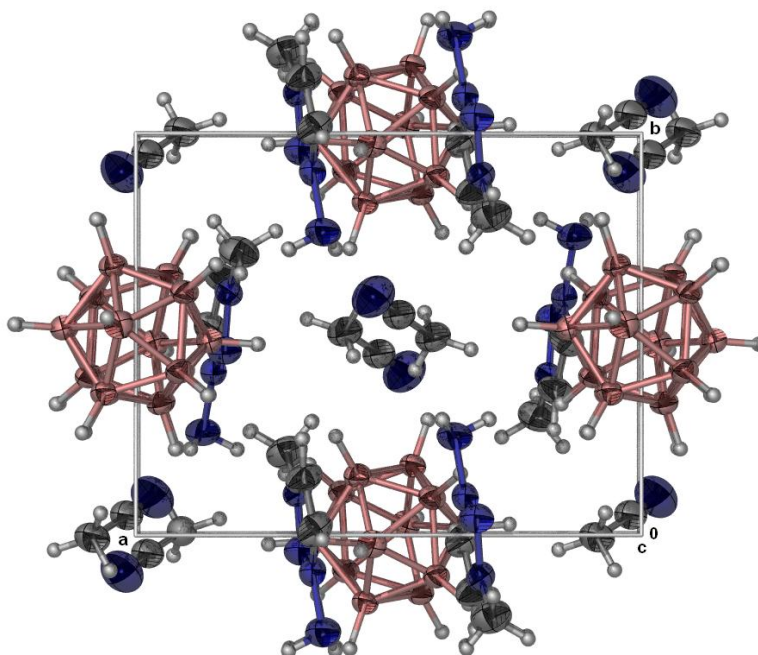
	(2·2CH <sub>3</sub> CN) (M1AT) <sub>2</sub> B <sub>12</sub> H <sub>12</sub> ·2CH <sub>3</sub> CN
Formula	B <sub>12</sub> H <sub>12</sub> 2(C <sub>3</sub> H <sub>7</sub> N <sub>4</sub> ), 2(C <sub>2</sub> H <sub>3</sub> N)
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> monoclinic
<i>a</i> (Å)	11.590(5)
<i>b</i> (Å)	8.959(4)
<i>c</i> (Å)	12.229(5)
β (°)	102.668(9)
<i>V</i> /Å <sup>3</sup>	1238.9(9)
ρ <sub>calc</sub> /g cm <sup>-3</sup>	1.132
<i>Z</i>	2
Formula weight	422.18
μ/mm <sup>-1</sup>	0.066
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.41x0.26x0.17
Theta range θ/°	2.19 to 28.19
Index range	-15≤ <i>h</i> ≤14, -9≤ <i>k</i> ≤11, -15≤ <i>l</i> ≤16
Reflection collected	12470
Independent [R(int)]/	2895 [0.0406]
Obs. refl. ([I > 2.0 σ(I)])	1676
F(000)	444
GooF	1.025
R <sub>1</sub> , wR [I > 2σ(I)]	0.0492, 0.1316
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.1066, 0.1567
L.diff. peak/hole eÅ <sup>-3</sup>	0.20 and -0.17
Absorption correct.	multiscan SADABS
T <sub>min</sub> , T <sub>max</sub>	0.973, 0.989
Data/restraints/param.	2895/0/209
Refinement method	Full-matrix least squares on F <sup>2</sup>

$$R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|; R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2)\}^{1/2}$$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure 3.** Molecular drawing of **2**. Thermal ellipsoids are shown at 50% probability level.



**Figure 4.** Crystal packing of **2** viewed along the *c*-axis.

**[1-Amino-3-H-1,2,3-triazolium]<sub>2</sub>[closo-B<sub>12</sub>H<sub>12</sub>] (3):** Solid [1-Amino-3-H-1,2,3-triazolium] chloride (3.01 g; 25.01 mmol prepared from the known<sup>18</sup> free base via treatment with ethanolic. HCl followed by recrystallization from 2-propanol) and commercial K<sub>2</sub>[closo-B<sub>12</sub>H<sub>12</sub>] (2.75 g; 12.50 mmol; limiting reagent) were placed into a 50 mL beaker. To this was added 6.0 mL DI water. The contents were stirred (glass stirring rod) and heated at reflux for 5 min on a hot plate. The resulting deep-red clear solution was cooled overnight in a refrigerator (3.5 °C) and massive ruby-red rhombs deposited. The crystals were stirred several times after crystallization began. Filtration of the crystals, rinsing the filter-cake with 1.0 mL of pre-chilled DI water, and drying to an amorphous powder by pumping for 72 h in a tarred flask at high vacuum (50 mTorr) with occasional application of a heat gun gave anhydrous beige-colored material that was spectroscopically homogenous by <sup>1</sup>H NMR (2.98 g; 76.4%). The decrease in water of hydration was readily followed by performing <sup>1</sup>H NMR on small aliquots of the drying solid. Purified material was obtained via dissolution in hot anhyd methanol (a small amount of KCl fails to dissolve and the supernatant is decanted into a clean flask), treatment with activated carbon, filtration through Celite, heating to reflux, and addition of ethyl acetate as the methanol gradually boiled away. The volume is reduced until oiling is imminent, and then one additional drop of anhydrous methanol is added. After seeding, cooling overnight in a freezer (-13.5 °C) gave straw-colored crystals, which were filtered with swirling, and pumped at high vacuum (50 mTorr) with periodic treatment with a heat gun. The product is relatively hygroscopic (and crystalline) but a trace of moisture can be removed under high vacuum in a Chem-Dry™ apparatus (held at 65 °C) over 72 h albeit with concomitant conversion of the crystals into an amorphous off-white powder; 2.38 g; overall yield from limiting reagent to pure substance = 61.1% (mp = 148-152 °C with gas



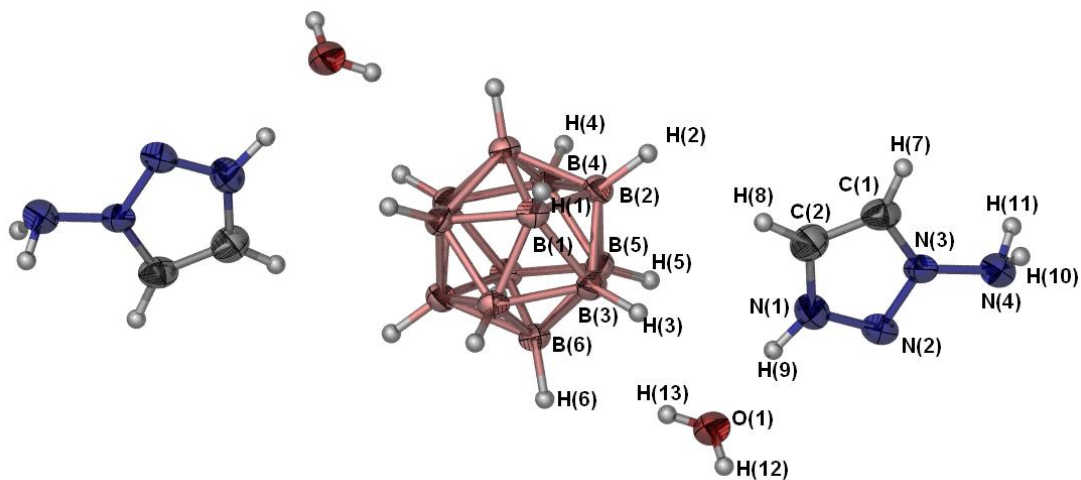
evolution):  $^1\text{H}$  NMR (400.132 MHz; DMSO- $d_6$  (center peak = 2.50)  $\delta$  9.72 (brs, 6H), 8.06 (s, 2H), 7.91 (s, 2H) 1.55-0.10 (complex unresolved m 12H);  $^{13}\text{C}$  NMR (100.624 MHz, decoupled, DMSO- $d_6$  (center peak = 39.51)  $\delta$  131.72, 124.71; FTIR (HATR method; significant peaks) 3722, 3694, 3624, 3583, 3534, 3297, 3220, 3154, 3126, 2492, 2451, 2431, 1679, 1589, 1544, 1462, 1397, 1295, 1262, 1152, 1115, 1074, 1054, 1013, 939, 882, 804, 760, 715, 698, 666, 629  $\text{cm}^{-1}$ .

**Table 3.** Crystal and structure refinement data for **3·2H<sub>2</sub>O**.

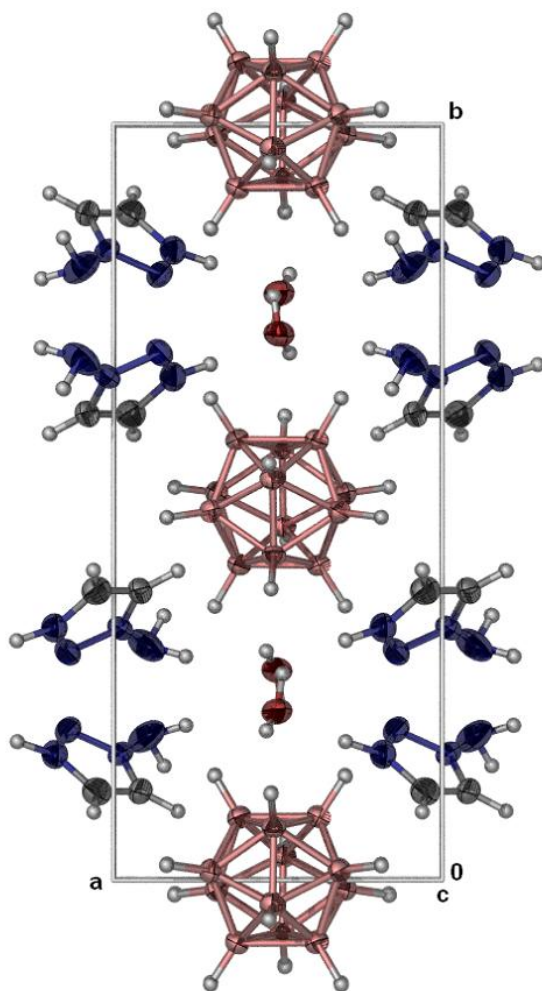
	(3·2H <sub>2</sub> O) (1ATH) <sub>2</sub> B <sub>12</sub> H <sub>12</sub> ·2H <sub>2</sub> O
Formula	B <sub>12</sub> H <sub>12</sub> , 2(C <sub>2</sub> H <sub>5</sub> N <sub>4</sub> ), 2(H <sub>2</sub> O)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> monoclinic
<i>a</i> (Å)	7.3950(5)
<i>b</i> (Å)	16.8827(12)
<i>c</i> (Å)	7.3580(7)
$\beta$ (°)	97.048(5)
<i>V</i> /Å <sup>3</sup>	911.69(12)
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.268
<i>Z</i>	2
Formula weight	348.05
$\mu/\text{mm}^{-1}$	0.629
Temperature (K)	296(2)
$\lambda(\text{CuK}\alpha)$	1.54178
Crystal size	0.38x0.24x0.31
Theta range $\theta$ /°	5.24 to 64.73
Index range	-8 $\leq h \leq$ 8, -13 $\leq k \leq$ 19, -5 $\leq l \leq$ 5
Reflection collected	3124
Independent [R(int)]/	958 [0.0254]
Obs. refl. ( $I > 2.0 \sigma(I)$ )	936
F(000)	364
GooF	1.087
<i>R</i> <sub>1</sub> , <i>wR</i> [ $I > 2\sigma(I)$ ]	0.0508, 0.1226
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0511, 0.1230
L.diff. peak/hole eÅ <sup>-3</sup>	0.21 and -0.57
Absorption correct.	multiscan SADABS
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.787, 0.860
Data/restraints/param.	958/0/171
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>

$$R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|; R_2 = \{\Sigma [w(|F_o|^2 - |F_c|^2)^2]/\Sigma (w(|F_o|^2)^2)\}^{1/2}$$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure 5.** Molecular drawing of **3**. Thermal ellipsoids are shown at 50% probability level.



**Figure 6.** Crystal packing of **3** viewed along the *c*-axis.

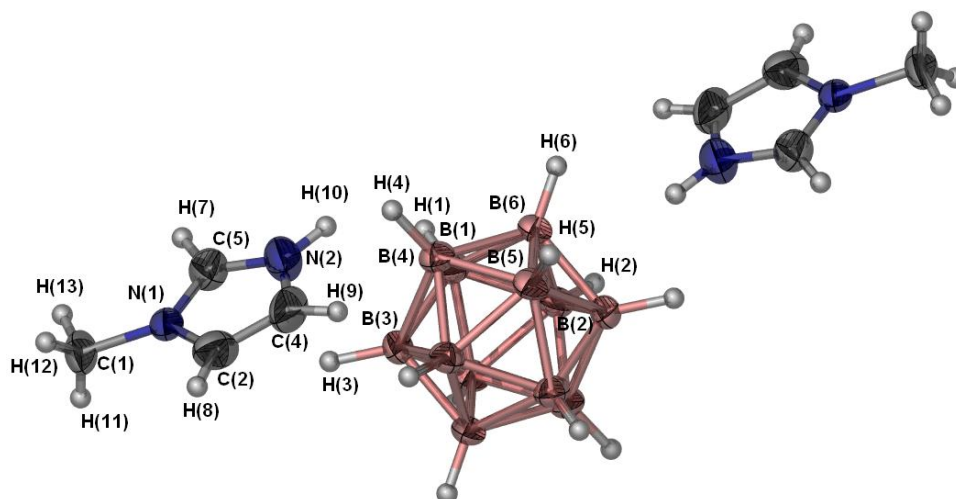
**[1-Methyl-3-H- imidazolium]<sub>2</sub>[*closo*-B<sub>12</sub>H<sub>12</sub>] (4):** Colorless oily [Methyl-1-H-imidazolium] chloride (2.66 g; 22.42 mmol; prepared in the same batch as above, from methylimidazole (Aldrich) plus 1.3 equiv. aq 12M HCl plus ethanol plus removal of volatiles) was weighed by difference into a 50 mL Pyrex beaker, diluted with 5.0 mL of DI water, and brought to *ca.* 60 °C on a hot plate. Simultaneously, a sample of K<sub>2</sub>[*closo*-B<sub>12</sub>H<sub>12</sub>] (2.20 g; 10.00 mmol) was added to a fresh 50 mL Pyrex beaker, diluted with 5.0 mL of DI water, and brought to *ca.* 60 °C on a hot plate. The chloride solution was added to the borane solution affording an immediate precipitate. The beaker that had contained the chloride was rinsed with 2 x 2.5 mL of DI water which was then added to the combined reagents. The metathesis reaction mixture was heated to gentle reflux and kept at reflux for a total of four minutes. The reaction mixture was cooled overnight in the refrigerator (3.5 °C), filtered, the solid rinsed with 3.0 mL of DI water, and the solid dried at high vacuum (50 mTorr) for several hours in a tared flask to provide a crude salt that was spectroscopically pure by <sup>1</sup>H NMR (2.53 g; 82.3%). Purified material was obtained by recrystallization of a sub-portion (1.17 g) from 36.0 mL of refluxing DI water followed by slow cooling overnight in the refrigerator (3.5°C). The crystals were filtered, rinsed with 2 x 3.0 mL portions of pre-chilled DI water, and volatiles removed by pumping overnight at high vacuum (40 mTorr) in a tared flask to give a white crystalline solid; 0.853g; recovery from the DI water recrystallized sub-portion = 72.9%; overall yield from initial limiting reagent to purified material = 60.0% (mp = 260-262 °C with gas evolution): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.51) δ 14.19 (brs, 2H), 9.02 (s, 2H), 7.70-7.64 (overlapping m {partially resolved} centered, 7.678, 7.667) dt, J = 4.4, 1.6 Hz, 4H), 3.87 (s, 6H), 1.70-0.10 (complex unresolved m, 12H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51) δ 135.74, 123.17, 119.73, 35.49; FTIR (HATR method; significant peaks) 3726, 3698, 3640, 3620, 3591, 3252, 3175, 3134, 3105, 3072, 3007, 2970, 2864, 2733, 2692, 2586, 2484, 2435, 2419, 2006, 1724, 1708, 1683, 1610, 1581, 1544, 1434, 1422, 1377, 1332, 1303, 1278, 1152, 1103, 1058, 1009, 911, 841, 747, 715, 666, 625 cm<sup>-1</sup>

**Table 4.** Crystal and structure refinement data for **4**.

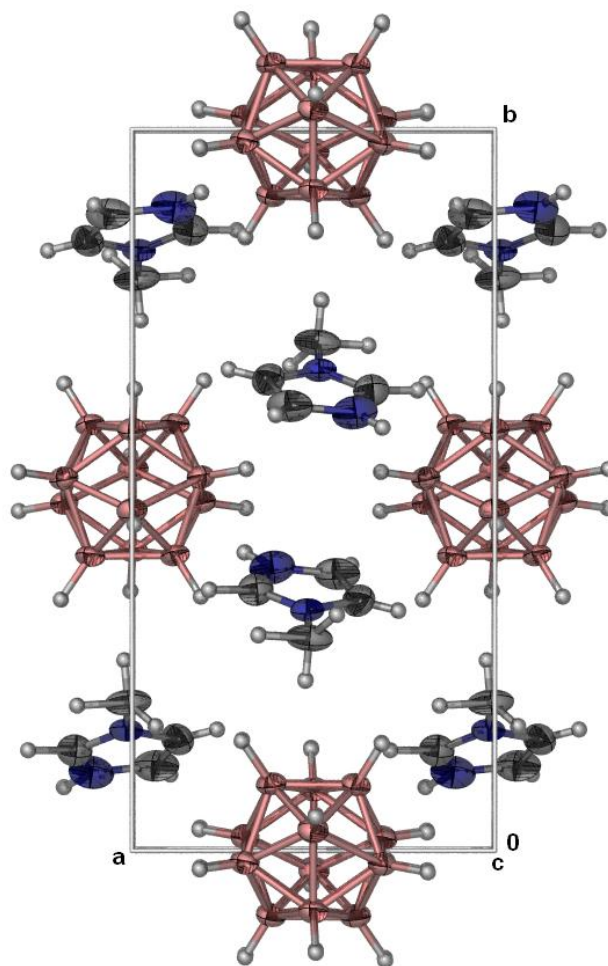
	(4) (MIMH) <sub>2</sub> B <sub>12</sub> H <sub>12</sub>
Formula	B <sub>12</sub> H <sub>12</sub> , 2(C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> )
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> monoclinic
<i>a</i> (Å)	7.535(4)
<i>b</i> (Å)	15.011(7)
<i>c</i> (Å)	8.168(4)
β (°)	90.329(7)
<i>V</i> /Å <sup>3</sup>	923.9(8)
ρ <sub>calc.</sub> /g cm <sup>-3</sup>	1.107
<i>Z</i>	2
Formula weight	308.05
μ/mm <sup>-1</sup>	0.058
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.42x0.11x0.08

Theta range $\theta/^\circ$	2.49 to 28.16
Index range	$-9 \leq h \leq 9$ , $-19 \leq k \leq 19$ , $-10 \leq l \leq 10$
Reflection collected	8736
Independent [R(int)]/	2050 [0.0611]
Obs. refl. ( $[I > 2.0 \sigma(I)]$ )	1397
F(000)	324
GooF	1.232
$R_1$ , $wR$ [ $I > 2\sigma(I)$ ]	0.0774, 0.1502
$R_1$ , $wR_2$ (all data)	0.1172, 0.1667
L.diff. peak/hole $e\text{\AA}^{-3}$	0.21 and -0.20
Absorption correct.	multiscan SADABS
$T_{\min}$ , $T_{\max}$	0.970, 0.995
Data/restraints/param.	2050/0/163
Refinement method	Full-matrix least squares on $F^2$
$R_1 = \Sigma   F_o  -  F_c   / \Sigma  F_o $ ; $R_2 = \{ \Sigma [w( F_o ^2 -  F_c ^2)^2] / \Sigma (w F_o ^2) \}^{1/2}$	

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure 7.** Molecular drawing of **4**. Thermal ellipsoids are shown at 50% probability level.



**Figure 8.** Crystal packing of **4** viewed along the *c*-axis.

**[1-Ethyl-3-methylimidazolium]<sub>2</sub>[closo-B<sub>12</sub>H<sub>12</sub>] (5):** A sample of [1-Ethyl-3-methylimidazolium] chloride (3.02 g; 20.63 mol, (Aldrich, hygroscopic) was quickly weighed out and transferred to a 50 mL Pyrex beaker containing 15.0 mL De water. To another 50 mL Pyrex beaker was added K<sub>2</sub>[closo-B<sub>12</sub>H<sub>12</sub>] (2.27 g; 10.31 mmol) dissolved in 15.0 mL of warm DI water. The borane solution was added to the chloride solution. The resulting suspension was allowed to gently reflux on the hot plate and the walls of the flask were rinsed with 15.0 mL of DI water. The suspension was again brought to a final gentle reflux for 2 min whereupon it partially clarified. Upon removal from the hot plate, immediate crystallization began. The growing mass of crystals in the beaker was cooled overnight in a refrigerator (3.5 °C). The crystals were filtered and washed with 4.0 mL of pre-chilled DeI water. The crystals were dried overnight at high vacuum (40 mTorr) to afford a fine white solid (3.07 g; 81.6%) that was spectroscopically pure by <sup>1</sup>H NMR. Purified material was obtained by recrystallization of a portion (1.13 g) in 60.0 mL of DI water and 5.0 mL of methanol at gentle reflux. Most of the methanol was allowed to boil away. The solution was allowed to slowly cool to room temperature and the resulting



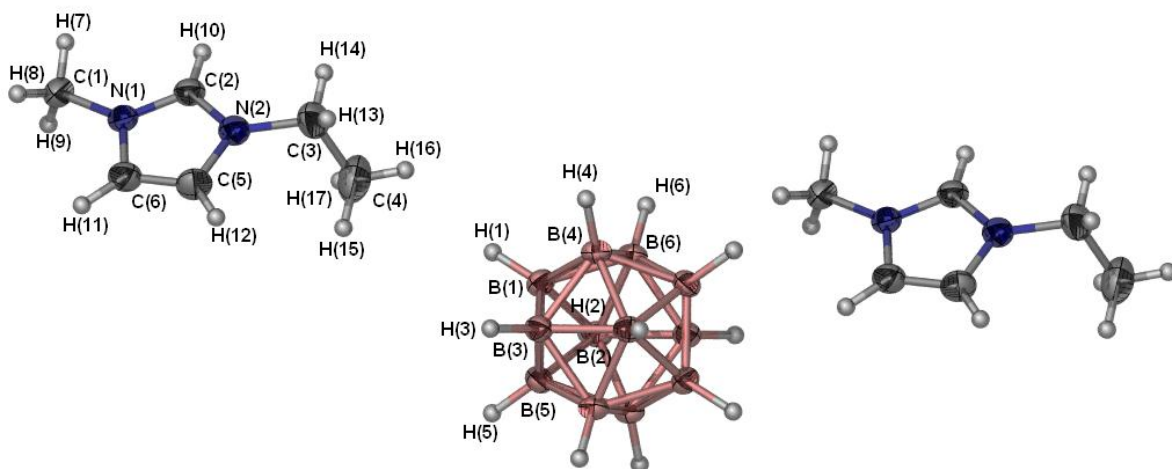
suspension of crystals was then cooled overnight in a refrigerator (3.5 °C). The crystals were filtered, rinsed with 4.5 mL of pre-chilled DI water, and then dried at high vacuum (50 mTorr) in a tared flask to provide a white solid; 1.02 g; recovery from DI water recrystallized sub-portion = 90.9%; overall yield from initial reagent to purified substance = 74.2% (mp = 290-292 °C with gas evolution): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.50) δ 9.08 (s, 2H), 7.78 (t, J = 1.8 Hz, 2H), 7.69 (t, J = 1.8 Hz, 2H), 4.20 (q, J = 7.2 Hz, 4H), 3.85 (3, 6H), 1.55-0.15 (complex unresolved m, 12H), 1.42 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51): δ 136.16, 123.52, 121.91, 44.16, 35.73, 15.15; FTIR (HATR method; significant peaks) 3354, 3150, 3113, 2987, 2950, 2480, 2443, 1724, 1622, 1569, 1499, 1471, 1446, 1242, 1168, 1136, 1119, 1058, 833, 782, 756, 715, 641, 612 cm<sup>-1</sup>; HRMS calcd for [M – C<sub>6</sub>H<sub>11</sub>N<sub>2</sub> – 2H]<sup>+</sup> 253.3051, found 253.3051.

**Table 5.** Crystal and structure refinement data for **5**.

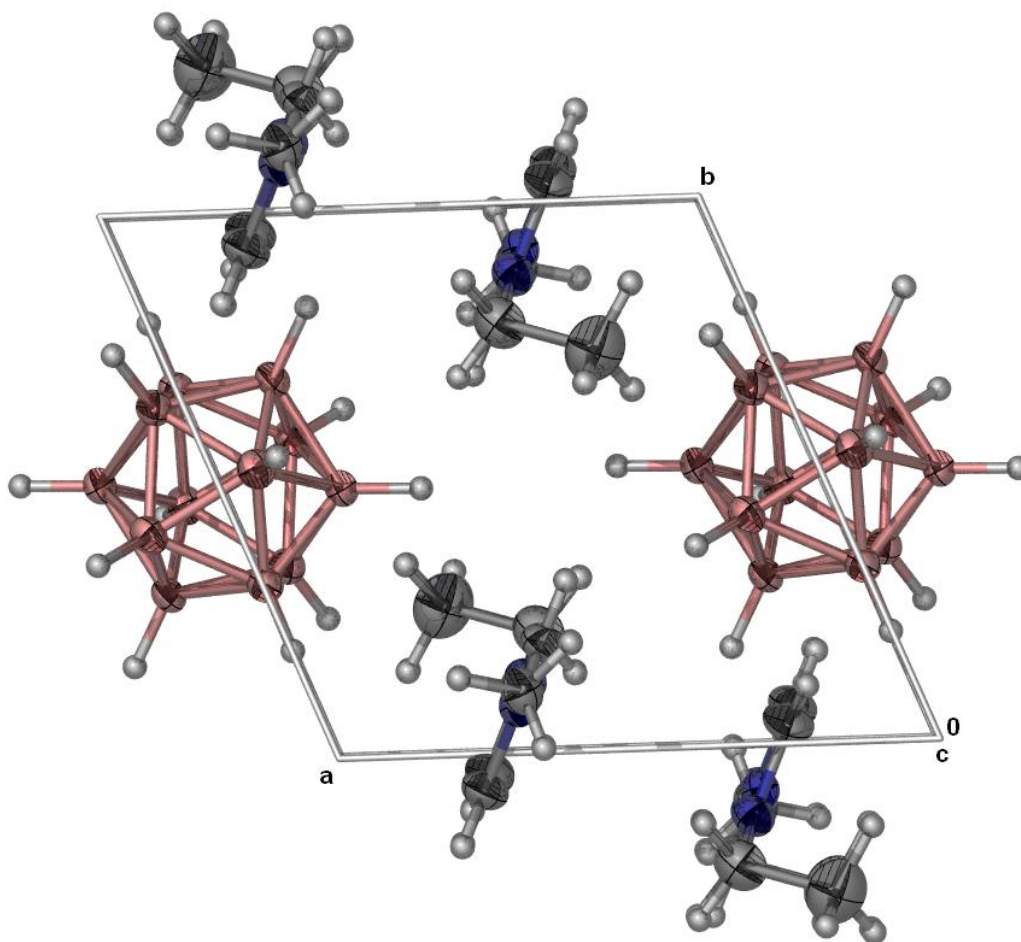
	(5) (EMIM) <sub>2</sub> B <sub>12</sub> H <sub>12</sub>
Formula	B <sub>12</sub> H <sub>12</sub> , 2(C <sub>6</sub> H <sub>11</sub> N <sub>2</sub> )
Space group	<i>P</i> -1 triclinic
a (Å)	8.2681(17)
b (Å)	8.6731(16)
c (Å)	8.8457(16)
α (°)	69.757(2)
β (°)	84.526(2)
γ (°)	67.5210(10)
V/Å <sup>3</sup>	549.43(18)
ρ <sub>calc</sub> /g cm <sup>-3</sup>	1.101
Z	1
Formula weight	364.15
μ/mm <sup>-1</sup>	0.058
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.38x0.27x0.16
Theta range θ/°	2.46 to 28.44
Index range	-10≤h≤10, -11≤k≤11, -11≤l≤11
Reflection collected	6117
Independent [R(int)]/	2514 [0.0335]
Obs. refl. ([I > 2.0 σ(I)])	2207
F(000)	194
GooF	1.078
R <sub>1</sub> , wR [I > 2σ(I)]	0.0495, 0.1451
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.0544, 0.1501
L.diff. peak/hole eÅ <sup>-3</sup>	0.20 and -0.21
Absorption correct.	Multiscan SADABS
T <sub>min</sub> , T <sub>max</sub>	0.978, 0.991
Data/restraints/param.	2514/0/196
Refinement method	Full-matrix least squares on F <sup>2</sup>

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; R_2 = \{ \sum [w(|F_o|^2 - |F_c|^2)^2] / \sum (w(|F_o|^2)^2) \}^{1/2}$$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure 9.** Molecular drawing of **5**. Thermal ellipsoids are shown at 50% probability level.



**Figure 10.** Crystal packing of **5** viewed along the *c*-axis.

**[4-Amino-1-H-1,2,4-triazolium][*closo*-CB<sub>11</sub>H<sub>12</sub>] (6):** Solid [4-Amino-1H-1,2,4-triazolium] chloride (1.81 g; 15.00 mmol, limiting reagent; made from commercial 4-amino-1,2,4-triazole free base (Aldrich) plus ethanolic HCl and recrystallized from EtOH/Et<sub>2</sub>O) and commercial K[*closo*-CB<sub>11</sub>H<sub>12</sub>] (2.74 g; 15.01 mmol) were placed in a 50 mL beaker containing 12.0 mL of DI water. The contents were stirred (glass stirring rod) and heated to reflux for 4 min on a hot plate. The resulting clear solution was drained into a fresh 50 mL beaker and the walls of the original beaker were rinsed with 1.5 mL of hot DI water (a very small amount (*ca.*, 20 mg) of an insoluble curd-like impurity remained behind in the original beaker – possibly a minor inorganic impurity in this commercial batch of K[CB<sub>11</sub>H<sub>12</sub>] since no peaks were observable in the semi-solubilized (DMSO-*d*<sub>6</sub>) curd via <sup>1</sup>H NMR). The clear solution was cooled overnight in a refrigerator (3.5 °C). Spar-like crystals grew after an initial partial oiling process. Once crystallization began, the suspension was stirred repeatedly during the cooling. Filtration was followed by rinsing with 1.0 mL of pre-chilled DI water. Drying overnight in a tarred flask at high vacuum (50 mTorr) gave an isolate that was spectroscopically pure by <sup>1</sup>H NMR (2.43 g; 71.0%). Recrystallization of the crude

solid by dissolving in 30.0 mL of DI water at reflux was followed by rinsing the clear solution into a fresh beaker. As before, a trace (*ca.* 5 mg) of curdy material remained behind on the walls of the first beaker. Slow cooling overnight to 3.5 °C, filtration and rinsing of the filter-cake with 1.0 mL of pre-chilled DI gave spar-like needles; 1.49 g; overall yield from initial limiting reagent to dried (via extended pumping at high vacuum (50 mTorr)) DI water recrystallized product = 43.5% (mp = 260-262°C): <sup>1</sup>H NMR (400.132 MHz; CD<sub>3</sub>CN (center peak = 1.94) δ 9.91 (brs, 1H), 8.95 (s, 2H), 5.85 (brs, 2H), 2.36 (brs, 1H), 2.25-0.75 (complex unresolved m 11H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51) δ 144.07, 50.86; FTIR (HATR method; significant peaks): 3346, 3305, 3285, 3248, 3199, 3130, 3060, 2987, 2570, 2513, 2496, 1638, 1593, 1548, 1511, 1487, 1462, 1450, 1205, 1131, 1086, 1058, 1025, 931, 870, 850, 792, 706, 670, 612 cm<sup>-1</sup>; HRMS calcd for [M – 3H]<sup>+</sup> 225.2314, found 225.2313; calcd for [HCB<sub>11</sub>H<sub>11</sub>]<sup>+</sup> 143.2035, found 143.2033.

**[4-Amino-1-methyl-1,2,4-triazolium][*closo*-CB<sub>11</sub>H<sub>12</sub>] (7):** Solid [4-Amino-1-methyl-1,2,4-triazolium] iodide (4.52 g; 20.00 mmol; limiting reagent; prepared from the free base as a tan solid by prolonged treatment with excess iodomethane in methanol (with protection from direct light) plus recrystallization from methanol) was placed in a 50 mL Pyrex beaker. To this was added commercial K[*closo*-CB<sub>11</sub>H<sub>12</sub>] (3.65 g; 20.02 mmol). The contents of the beaker were diluted with 32.0 mL of DI water and brought to a gentle reflux for two min. The solution was transferred to a clean 50 mL Pyrex beaker (thereby leaving behind a trace (*ca.* 20 mg) of a curdy insoluble residue). The reaction mixture was kept overnight in a refrigerator (3.5 °C). Copious precipitation of an off-white solid occurred. The salt was filtered, rinsed with 6.0 mL of pre-chilled DI water, and pumped at high vacuum (40 mTorr) in a tared flask. This gave a solid (4.46 g; 92.0%) that was spectroscopically pure by <sup>1</sup>H NMR (although a trace of water was present). Purified material was obtained by recrystallizing a sub-portion (1.28 g) of the crude isolated product from 50.0 mL of gently refluxing DI water, cooling overnight in a refrigerator (3.5 °C), filtering, and rinsing with 2.0 mL of pre-chilled DI water. The white crystals were pumped in a tared flask at high vacuum (40 mTorr) to afford a dry solid; 0.912 g; recovery from DI recrystallized recrystallized sub-portion = 71.2%; overall yield from initial limiting reagent to purified substance = 65.5% (mp = 161-162°C): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.50) δ 10.08 (s, 1H), 9.16 (s, 1H), 6.96 (s, 2H), 4.03 (s, 3H), 2.40 (brs, 1H), 2.25-0.075 (complex unresolved m, 11H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51) δ 145.03, 142.95, 50.75, 38.88; FTIR (HATR method; significant peaks) 3350, 3289, 3248, 3142, 3101, 2982, 2529, 2480, 2120, 1626, 1581, 1479, 1446, 1205, 1168, 1127, 1091, 1066, 1021, 919, 862, 784, 715, 666, 608 cm<sup>-1</sup>; HRMS calcd for [M – 3H]<sup>+</sup> 239.2471, found 239.2470; calcd for [HCB<sub>11</sub>H<sub>11</sub>]<sup>+</sup> 143.2035, found 143.2037.

**[1-Amino-3-methyl-1,2,3-triazolium][*closo*-CB<sub>11</sub>H<sub>12</sub>] (8):** Solid [1-Amino-3-methyl-1,2,3-triazolium] iodide (4.79 g; ≤ 21.19 mmol; generated from the known<sup>18</sup> 1-amino-1,2,3-triazole free base by reaction at room temperature with excess iodomethane in ethanol {in a flask protected by Al foil from direct light} followed by prolonged pumping off of the volatiles at high vacuum {60 mTorr} to generate a crude dark red solid whose <sup>1</sup>H NMR was consistent with the desired structure; this was used without further purification; this served as the limiting reagent) was weighed into a 50 mL Pyrex beaker. To this was added commercial K[*closo*-CB<sub>11</sub>H<sub>12</sub>] (4.03 g; 22.13 mmol). The contents of the beaker were diluted with 25 mL of DI water and the mixture was heated at gentle reflux for 3 min.

Unlike results seen for another batch of commercial K[*closo*-CB<sub>11</sub>H<sub>12</sub>], this batch of carborane gave a metathesis reaction mixture that was completely devoid of any curdy precipitate on the walls of the hot beaker. Upon cooling overnight in a refrigerator (3.5 °C), a copious mass of solid deposited. The crystals were filtered, rinsed with 3.0 mL of pre-chilled DI water, and pumped at high vacuum (50mTorr) in a tared flask to give spectroscopically pure (by <sup>1</sup>H NMR) solid (4.92 g; 95.8%). From pooled batches of this semi-pure salt (4.92 g), recrystallization from refluxing DI water (30.0 mL) and methanol (20.0 mL), with removal of most of the more volatile methanol during the boiling process, followed by cooling overnight in the refrigerator (3.5 °C) gave pure material; 3.94 g; recovery from this recrystallization = 79.9%; overall yield from initially limiting reagent to pure material = 76.5% (mp = 259-262°C): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.50) δ 8.74 (d, J = 1.2 Hz, 1H), 8.60 (d, J = 1.2 Hz, 1H), 8.28 (brs, 2H), 4.21 (s, 3H), 2.39 (brs, 1 H), 2.25-0.75 (complex unresolved m, 11H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51): δ 131.55, 126.82, 50.75, 39.66; FTIR (HATR method; significant peaks): 3726, 3698, 3624, 3596, 3342, 3273, 3158, 3138, 2517, 1650, 1605, 1536, 1479, 1442, 1397, 1315, 1230, 1209, 1091, 1058, 1021, 890, 780, 719, 666, 633 cm<sup>-1</sup>; HRMS calcd for [M – 3H]<sup>+</sup> 239.2471, found 239.2477; calcd for [HCB<sub>11</sub>H<sub>11</sub>]<sup>+</sup> 143.2035, found 143.2040.

**[1-Amino-3-H-1,2,3-triazolium][*closo*-CB<sub>11</sub>H<sub>12</sub>] (9):** Solid [1-Amino-3-H-1,2,3-triazolium] chloride (2.41 g; 20.00 mmol; limiting reagent; made from the free base<sup>19</sup> by reaction with aq conc. HCl in ethanol followed by pumping off volatiles at high vacuum (50 mTorr) followed by recrystallization from a minimum volume of refluxing isopropanol, and commercial K[*closo*-CB<sub>11</sub>H<sub>12</sub>] (3.64 g; 20.01 mmol) are transferred to a 50 mL Pyrex beaker. Addition of 10 mL DI water was followed by heating to gentle reflux and then pouring the nearly clear solution into a fresh 50 mL Pyrex beaker. The decanting process left behind a small amount (*ca.* 15 mg) of a water insoluble curdy impurity that originates in the commercial carborane salt. The reaction mixture was cooled overnight in the refrigerator (3.5 °C). Filtration of the solid, rinsing of the precipitate with 2.0 mL of pre-chilled DI water, and pumping at high vacuum (60 mTorr) provided a crude solid (~4.59 g; slightly over theory due to entrained moisture). Two consecutive recrystallizations (each from 7.0 mL) of refluxing DI water gave a slightly impure first crystallite (70.8%) and, then, after the second recrystallization, essentially pure material; 2.51 g; overall yield for initial precipitation followed by two DI water recrystallizations = 54.9% (mp. = 182-183 °C with rapid gas evolution): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.50): δ 8.71 (brs, 3H), 7.96 (d, J = 1.1 Hz, 1H), 7.74 (d, J = 1.1 Hz, 1H), 2.39 (brs, 1H), 2.25-0.75 (complex unresolved m, 11H); <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51): δ 132.09, 124.28, 50.79; FTIR (HATR method; significant peaks) 3714, 3694, 3653, 3636, 3346, 3264, 3154, 3134, 2521, 1659, 1605, 1540, 1462, 1442, 1299, 1168, 1111, 1078, 1017, 956, 890, 788, 711, 694, 657, 625, 600, 564, 543 cm<sup>-1</sup>; HRMS calcd for [M – 3H]<sup>+</sup> 225.2315, found 225.2325; calcd for [HCB<sub>11</sub>H<sub>11</sub>]<sup>+</sup> 143.2035, found 143.2045.

**[1-Methyl-3-H-imidazolium][*closo*-CB<sub>11</sub>H<sub>12</sub>] (10):** Colorless oily [3-Methyl-1-H-imidazolium] chloride (2.608 g; 22.00 mmol; prepared from methylimidazole (Aldrich) plus 1.3 equiv. aq 12M HCl plus ethanol followed by prolonged pumping at high vacuum (40 mTorr) plus periodic moderate heating with a heat gun to achieve constant weight; the <sup>1</sup>H



NMR of the crude oil was reasonably clean and no further purification was done; a weighed excess of the liquid intermediate was used to ensure that a slight excess of chloride stoichiometry versus the potassium carborane salt was achieved) was weighed out by difference, transferred to a 50 mL Pyrex beaker, and diluted with 8.0 mL of hot DI water. A sample of commercial K[*closo*-CB<sub>11</sub>H<sub>12</sub>] (3.646 g; 20.02 mmol; limiting reagent) was dissolved in 8.0 mL of hot DI water. The chloride solution was added to the carborane solution and the chloride beaker was rinsed with 4.0 mL of hot DI water. The contents of the metathesis reaction beaker were brought to a gentle reflux and held at reflux for two minutes whereupon the clear solution was transferred to a fresh 50 mL Pyrex beaker. The final transfer of the metathesis reaction mixture was done to leave behind a trace (*ca.* 15 mg) of a curdy precipitate apparently caused by an inorganic insoluble impurity present in the commercial potassium carborane. The final beaker was allowed to stand for two days in the refrigerator (3.5 °C). The copious precipitate was filtered, rinsed with 3 x 2.0 mL of pre-chilled DI water, and pumped at high vacuum (50 mTorr) in a tared flask. This afforded chalky material that was spectroscopically pure by <sup>1</sup>H NMR (4.220 g; 93.2%). Purified material was obtained by recrystallization of a sub-portion (1.118 g) of the crude solid via dissolution in 35.0 mL of boiling DI water, performing a quick gravity filtration thru coarse filter paper and slowly cooling overnight in a refrigerator (3.5 °C). The crystals were filtered, rinsed with 1.5 mL of pre-chilled DI water, and dried in a tared flask at high vacuum (40 mTorr). There was obtained a white crystalline solid; 1.003 g; recovery from DI water recrystallized sub-portion = 89.7%; overall yield from initial limiting reagent to purified compound = 83.5% (mp = 368-369 °C): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.51): δ 14.17 (brs, 1H), 9.04 (s, 1H), 7.69 (brt, J = 1.6 Hz, 1H), 7.66 (brt, J = 1.6 Hz, 1H), 3.87 (s, 3H), 2.40 (brs, 1H), 2.25-0.70 (complex unresolved m, 11H). <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51): δ 135.80, 123.14, 119.75, 50.75, 35.44. FTIR (HATR method; significant peaks): 3722, 3698, 3620, 3587, 3362, 3150, 3138, 3105, 2521, 1605, 1577, 1544, 1434, 1372, 1328, 1303, 1274, 1144, 1082, 1021, 1009, 911, 833, 747, 711, 690, 666, 612, 555 cm<sup>-1</sup>; HRMS calcd for [M – 3H]<sup>+</sup> 223.2409, found 223.2408; calcd for [HCB<sub>11</sub>H<sub>11</sub>]<sup>+</sup> 143.2035, found 143.2037.

**[1-Ethyl-3-methylimidazolium][*closo*-CB<sub>11</sub>H<sub>12</sub>] (11):** Solid [1-Ethyl-3-methylimidazolium] chloride (2.710 g; 18.48 mmol; limiting reagent; Aldrich; hygroscopic) was weighed by difference and transferred into a 50 mL Pyrex beaker. To this was added commercial K[*closo*-CB<sub>11</sub>H<sub>12</sub>] (3.370 g; 18.50 mmol) followed by 30.0 mL of DI water. The contents were stirred (glass stirring rod) and the mixture was brought to gentle reflux for three minutes. The reaction mixture was transferred to a fresh 50 mL Pyrex beaker (a very small curdy deposit remained behind (~15 mg)) and the first beaker was rinsed with 15.0 mL of RT DI water. The reaction mixture was again brought to reflux for 2 min and the clear yellow solution was allowed to cool overnight in refrigerator (3.5 °C). The resulting crystals were filtered and washed with 5.0 mL of pre-chilled DI water. Drying overnight at high vacuum (40 mTorr), gave an off-white solid that was spectroscopically homogenous by <sup>1</sup>H NMR (4.400 g; 93.6%). Recrystallization of a portion (1.510 g) of the crude salt was by dissolution in 6.0 mL of DI water and 12.0 mL of methanol at reflux (with slow removal of most of the methanol by boiling), a quick gravity filtration, and slow crystallization overnight in a refrigerator (3.5 °C). Filtering, washing with 2.0 mL of pre-chilled DI water, and drying at high vacuum (40 mTorr) gave white crystals; 1.121 g; recovery from the DI water recrystallized sub-portion = 74.2%; overall yield from the initial limiting reagent to

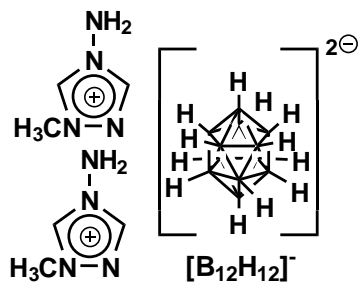
purified metathesis product = 69.5% (mp = 175-176 °C<sup>15</sup> with gas evolution): <sup>1</sup>H NMR (400.132 MHz, DMSO-d<sub>6</sub> (center peak = 2.50): δ 9.12 (s, 1H), 7.78 (t, J = 1.6 Hz, 1H), 7.69 (t, J = 1.6 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.40 (brs, 1H), 2.30-0.70 (complex unresolved m, 11H), 1.42 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100.624 MHz, decoupled, DMSO-d<sub>6</sub> (center peak = 39.51): δ 136.20, 123.56, 121.96, 50.72, 44.14, 35.70, 15.10. FTIR (HTAR method, significant peaks ): 3354, 3224, 3162, 3146, 3101, 2982, 2517, 2120, 2075, 1994, 1851, 1814, 1781, 1761, 1724, 1663, 1593, 1573, 1479, 1462, 1446, 1164, 1086, 1054, 1017, 927, 833, 784, 739, 711, 674, 662, 621, 592, 564 cm<sup>-1</sup>; HRMS calcd for [M – 3H]<sup>+</sup> 251.2722, found 251.2723; calcd for [HCB<sub>11</sub>H<sub>11</sub>]<sup>+</sup> 143.2035, found 143.2039.

Detailed visual melting point behavior for all product salts (**1–11**) is presented in Supplemental Table 1. These values were determined as follows: First, a run was made at a 10 °C/minute temperature rise to obtain an approximate melting point value for each salt sample; then, a second run was made with each salt sample using a 1 °C/minute temperature rise beginning about 20 °C below the initial melt response. Finally, a third melting point run was conducted for each sample using another 1 °C/minute temperature rise which was begun about 10 °C below the initial melt shown by the second run.

This third run data was used to establish the published melting point or decomposition temperature values (**Table 6**) from iteratively comparing visual observations of each sample directly in the apparatus melting point compartment and the resultant video replay of that same sample. Softening means that the crystalline salt appeared to lose its sharp crystalline character to a more velvet-like solid that was devoid of sharp corners on the solid particles. Sinters denotes that the crystals lost their sharp crystalline character as the softened material rapidly shrunk (decreased) in volume before melting (liquefaction) visually was observed.

**Table 6.** Melting Point Data Determined with the SRS MPA100 Apparatus.

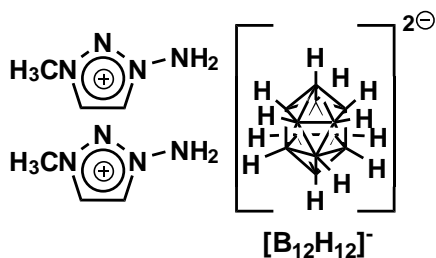
# DETAILED MELTING POINT DATA (°C)



1

SINTERS 180.2 - 180.6

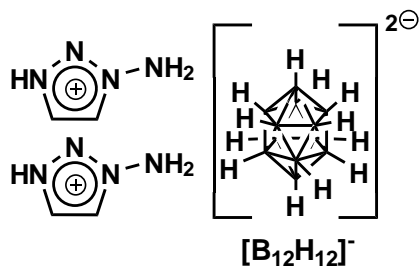
MELTS 180.7 - 181.7 to colorless liquid



2

SOFTENS 193.5 - 197.7

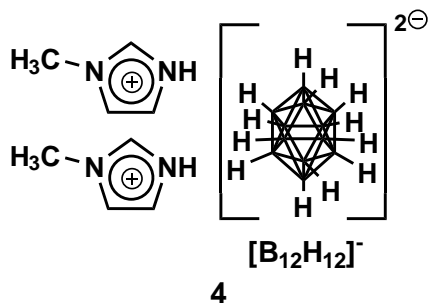
MELTS with slow gas evolution 198.7 - 218.1  
leaving a colorless liquid



3

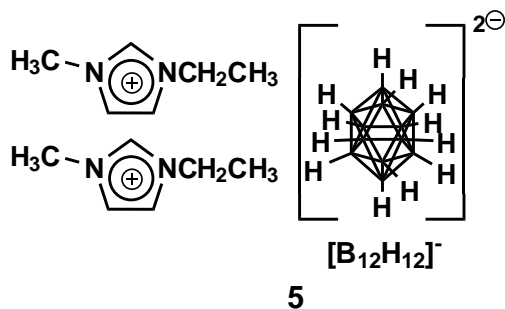
SOFTENS 145.6 - 147.2

MELTS with gas evolution 147.8 - 152.0  
leaving a translucent residue



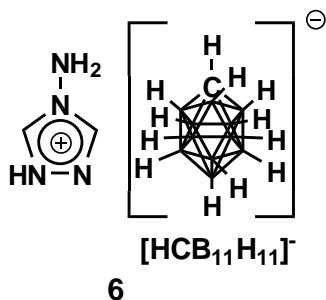
**SOFTENS 257.8 - 259.3**

**MELTS with gas evolution 259.7 - 261.6**  
leaving a colorless liquid



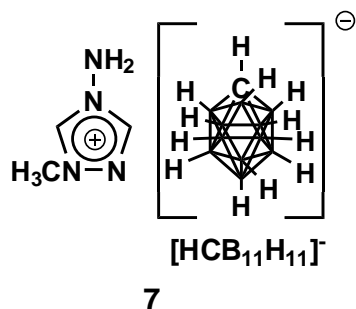
**SOFTENS 285.8 - 289.4**

**MELTS with gas evolution 289.7 - 292.5**  
leaving a colorless liquid



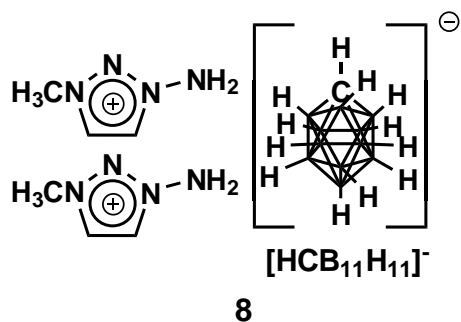
**SOFTENS 258.4 - 260.4**

**MELTS 260.5 - 261.8 to a light brown clear liquid**



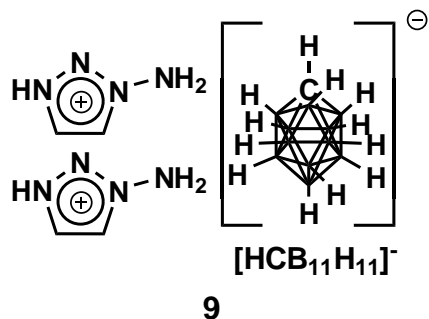
**SINTERS 158.5 - 160.8**

**MELTS 161.2 - 162.3 to a colorless liquid**



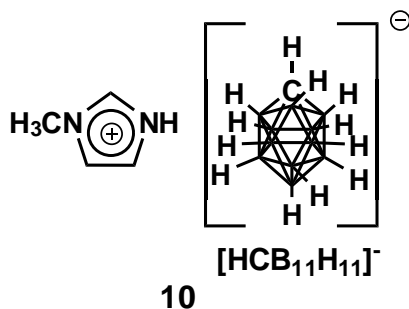
**SOFTENS 254.7 - 258.6**

**MELTS 258.9 - 261.7 to a clear brown liquid**



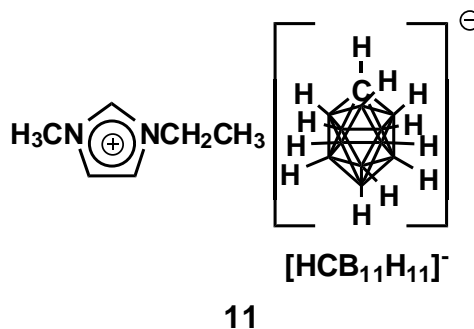
**SOFTENS / SINTERS (None Observed)**

**MELTS with rapid gas evolution 181.7 - 182.9  
leaving a clear brown liquid**



**SOFTENS 367.2 - 368.0**

**MELTS with gas evolution 368.1 - 369.0  
leaving a colorless liquid**



**SOFTENS 174.5 - 175.0**

**MELTS with gas evolution 175.2 - 176.5  
leaving a colorless liquid**